Spectrophotometric Studies on Organometallic Complexes Used in Analytical Chemistry. VIII : Composition and Formation Constant of Uranyl-Flavonol Complex

Spectrophotometric Studies on Organometallic Complexes Used in Analytical Chemistry. VIII. Composition and Formation Constant of Uranyl-Flavonol Complex

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Synopsis

The composition and the formation constant of uranyl-flavonol complex were studied spectrophotometrically by means of McConnell's method. From the results, it was clear that two species of the complex exist, the composition of which can be represented as UO_2Fl^+ and UO_2Fl_2. The first and second formation constants of uranyl-flavonol complex, k_1 and k_2, were observed to be $2.2_0\times10^{10}$ and $9.1_7\times10^8$ respectively, and therefore, the overall formation constant can be represented as 2.0×10^{19}. The dissociation constant of flavonol was observed spectrophotometrically to be $5.6_2\times10^{-11}$.

The uranyl-flavonol complex can be extracted in TBP as UO_2Fl_2. nTBP.

I. Introducion

In the previous paper[1], uranium was determined by extraction with a TBP-n-hexane solution of flavonol. The molecular absorption coefficient of the uranyl-flavonol complex formed under optimum condition was 28,700. In this paper, therefore, the composition and formation constant of this complex has been studied spectrophotometrically by means of McConnell's method[2].

II. Experiment

In this study, a 60% acetone solution was used as a solvent, and the ionic strength was fixed at 0.1 with sodium perchlorate, and the temperature was kept at 15°C.

Absorbancies were measured with Hitachi EPU-2 spectrophotometer and 10 mm cells, and pHs of solutions were measured with Beckman Model G glass electrode pH meter.

III. Acid dissociation constant of flavonol

The acid dissociation constant of flavonol was studied spectrophotometrically by the method which had been used by Hildebrand[3]. The structural formula and dissociation equilibrium are shown in Fig. 1. Absorption curves of flavonol at

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1) T. Kanno, Bunseki Kagaku, **8** (1959), 714.
2) H. McConnell and N. Davidson, J. Am. Chem. Soc., **72** (1950), 3164.
3) G. P. Hildebrand and C. N. Reilley, Anal. Chem., **29** (1957), 258.

various pH are shown in Fig. 2. As pH became higher, another absorption band grew, and the fixed absorption curve was obtained above pH 12.

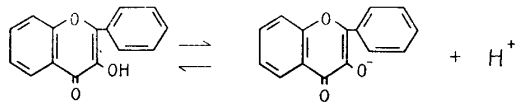

Fig. 1 Dissociation equilibrium of flavonol.

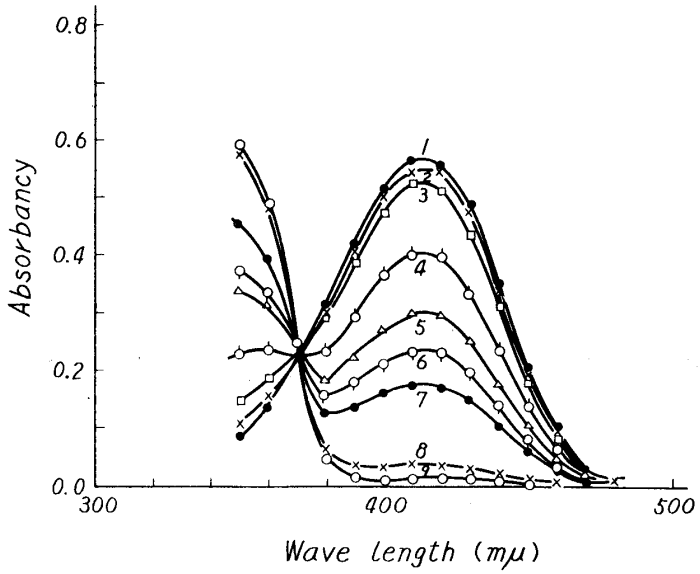

Fig. 2. Absorption curves of flavonol at different pHs.
Acetone 60 %, $NaClO_4$ 0.1 mol/l

Curve	1	pH>12.1	Curve	6	pH 10.2
〃	2	pH 11.7	〃	7	〃 9.9
〃	3	〃 11.1	〃	8	〃 9.3
〃	4	〃 10.6	〃	9	pH<7.5
〃	5	〃 10.4			

If HF1 represents flavonol, its dissociation equilibria and equilibrium constant are expressed by

$$HFl = H^+ + Fl^-, \tag{1}$$

$$K_a = \frac{[H^+]\,[Fl^-]}{[HFl]} . \tag{2}$$

From Eq. (2), the following relationship is obtained:

$$pH = p\,K_a - \log \frac{[HFl]}{[Fl^-]} . \tag{3}$$

A straight-line relationship, therefore, would be observed between pH and log ([HF1]/[Fl⁻]) from Eq. (3). For log ([HF1]/[Fl⁻])= 0, Eq. (3) is simplified as $pH = pK_a$.

In Fig. 3, log ([HFl]/[Fl⁻]) calculated from absorbancies of flavonol at 410 mμ was plotted against pH, and from this figure it was observed that pK_a is 10.25,

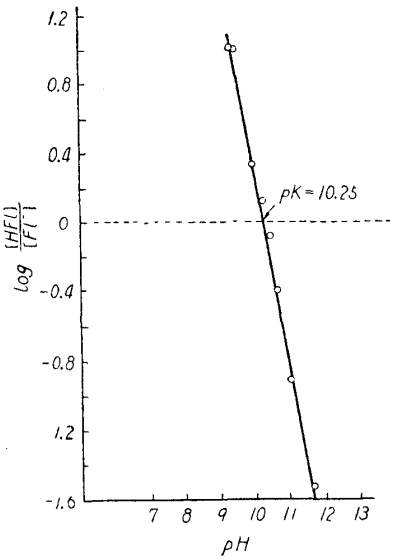

Fig. 3. Determination of dissociation constant of flavonol, Acetone 60%, $NaClO_4$ 0.1mol/l.

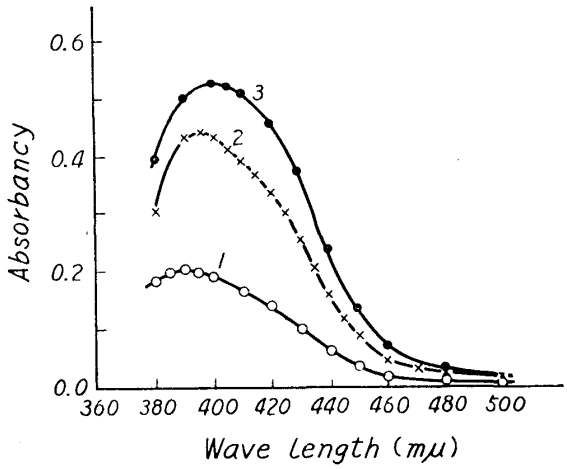

Fig. 4. Absorption curves of uranyl-flavonol chelate at different pHs.
Curve 1 pH 2.9 Curve 2 pH 4.2
Curve 3 pH 6.5

and then, K_a is $5.6_2\times10^{-11}$. The tangent of its line was about 1.

IV. Composition and formation constant of uranyl-flavonol complex

The absorption curves of uranyl-flavonol complexes obtained at pHs 2.9, 4.1 and 6.5 are shown in curves 1, 2, and 3 in Fig. 4 respectively. At about pH 2.9, the absorption curve has an absorption maximum at about 390 mμ, and it has an absorption maximum at about 400 mμ at pH 6.5. From these curves, it is seen that two species of uranyl-flavonol complex exist. At pH 4.2, it seems that two species of uranyl-flavonol complex coexisted. The compositions and formation constants of these complexes were studied by McConnell's method.

1. Uranyl-flavonol complex formed at pH 3.0

If $UO_2Fl_n^{-(n-2)}$ is the complex formed at pH 3.0, its formation equation is expressed as follows:

$$UO_2^{2+} + n\mathrm{HFl} = UO_2\,Fl_n^{-(n-2)} + n\mathrm{H}^+.$$

Then, equilibrium constant K_1 is

$$K_1 = \frac{[UO_2Fl_n^{-(n-2)}]\,[H^+]^n}{[UO_2^{2+}]\,[HFl]^n}.$$

If pH is fixed at constant value,

$$K_1' = \frac{K_1}{[H^+]^n} = \frac{[UO_2\,Fl_n^{-(n-2)}]}{[UO_2^{2+}]\,[HFl]^n}.$$

When the total concentrations of uranium and flavonol are a and b mol/1 re-

spectively, and the concentration of complex is x mol/l and $b \gg a$,

$$K_1' = \frac{x}{(a-x)\,(b-nx)^n} = \frac{x}{(a-x)b^n} . \tag{4}$$

A, the absorbancy observed, is expressed by the following relationship:

$$A = \varepsilon_1 x + \varepsilon_0 (b - nx),$$

where, ε_1 and ε_0 represent the molecular absorption coefficients of flavonol and complex respectively. Since the absorbancy of flavonol added, A', is $\varepsilon_0 b$, if the difference between the total absorbancy observed and the absorbancy of total flavonol is expressed as A_0, the following relationship is obtained:

$$A_0 = A - A' = (\varepsilon_1 - n\varepsilon_0)\, x.$$

When ε_0 is negligible with respect to ε_1, this equation is simplified as follows:

$$A_0 = \varepsilon_1 x. \tag{5}$$

By combining Eqs. (4) and (5), the following relationship is obtained:

$$A_0 = \varepsilon_1 \times \frac{ab^n K_1'}{K_1' b^n + 1} .$$

Then, the following relationship is obtained:

$$\frac{a}{A_0} = \frac{1}{\varepsilon_1} + \frac{1}{K_1' \varepsilon_1} \times \frac{1}{b^n} . \tag{6}$$

From this equation, it is to be expected that there is a straight-line relationship between a/A_0 and $1/b^n$. Fig. 5 represents the results obtained under the condi-

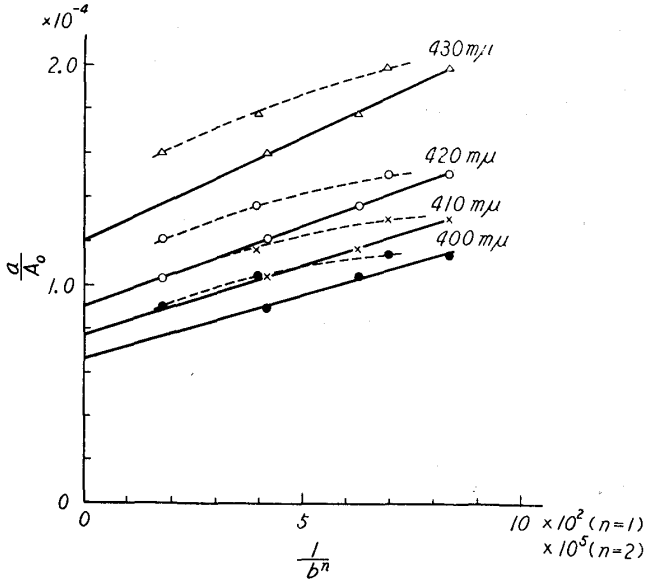

Fig. 5. Relation between a/A_0 and $1/b_n$ at pH 3.0.
Acetone 60%, $NaClO_4$ 0.1 mol/l
U 2.11×10^{-5} mol/l
Flavonol 1.20×10^{-3} mol/l, 1.60×10^{-3} mol/l, 2.40×10^{-3} mol/l

tion in which the concentration of uranium was fixed at 2.11×10^{-5} mol/1, the concentrations of flavonol were varied as 2.40×10^{-3}, 1.60×10^{-3} and 1.20×10^{-3} mol/1, and pH was fixed at 3.0. From this figure, it was observed that at n=1, straight-line relationships were obtained at 400, 410, 420 and 430 mμ, but at $n=2$, each line was curved. From the results, it was recognized that the complex formed at pH 3.0 was UO_2Fl^+ and ε_1 at 400 mμ was 14,700. From Eq. (6), K_1 was calculated as $1.2_3\times10^3$. The first formation constant was calculated as follows:

$$k_1 = \frac{[UO_2Fl^+]}{[UO_2^{2+}]\,[Fl^-]} = \frac{K_1'\,[H^+]}{K_a} = 2.2_0\times10^{10} \quad .$$

2. Uranyl-flavonol complex formed at pH 6~7

From Fig. 4, it is seen that another species exists at pH 4.2. If two species of complex, UO_2Fl^+ and $UO_2Fl_n^{-(n-2)}$, exist, the reactions are represented as follows:

$$UO_2^{2+} + HFl = UO_2Fl^+ + H^+, \tag{7}$$

$$UO_2Fl^+ + (n-1)\,HFl = UO_2Fl_n^{-(n-2)} + (n-1)\,H^+. \tag{8}$$

When equilibrium constants of Eqs. (7) and (8) are K_1 and K_2 respectively, they will be as follows:

$$K_1 = \frac{[UO_2Fl^+]\,[H^+]}{[UO_2^{2+}]\,[HFl]}\,, \tag{9}$$

$$K_2 = \frac{[UO_2Fl_n^{-(n-2)}]\,[H^+]^{n-1}}{[UO_2Fl^+]\,[HFl]^{n-1}}\,. \tag{10}$$

If the total concentrations of uranium and flavonol, and the concentrations of $UO_2\,Fl^+$ and $UO_2Fl_n^{-(n-2)}$ are a, b, x, and y mol/1 respectively, and if $b\gg a$, at a fixed pH, the following equations are obtained:

$$K_1' = \frac{K_1}{[H^+]} = \frac{[UO_2Fl^+]}{[UO_2^{2+}]\,[HFl]} = \frac{x}{(a-x-y)\,(b-x-ny)} = \frac{x}{(a-x-y)\,b}\,, \tag{11}$$

$$K_2' = \frac{K_1}{[H^+]^{n-1}} = \frac{[UO_2Fl_n^{-(n-2)}]}{[UO_2Fl^+]\,[HFl]^{n-1}} = \frac{y}{x\,(b-x-ny)^{n-1}} = \frac{y}{xb^{n-1}}\,. \tag{12}$$

By combining Eqs. (11) and (12), we have

$$x = \frac{K_1'ab}{1 + K_1'b + K_1'K_2'b^n}\,, \tag{13}$$

$$y = \frac{K_1'K_2'ab^n}{1 + K_1'b + K_1'K_2'b^n}\,. \tag{14}$$

If molecular absorption coefficients of flavonol, UO_2Fl^+ and $UO_2Fl_n^{-(n-2)}$ are ε_0, ε_1 and ε_2 respectively, A, the absorbancy observed is expressed as follows:

$$A = \varepsilon_1 x + \varepsilon_2 y + \varepsilon_0 (b - x - ny).$$

Since $A' = \varepsilon_0 b$ when A' represents the absorbancy of b mol/l flavonol solution, then

$$A_0 = A - A' = (\varepsilon_1 - \varepsilon_0) x + (\varepsilon_2 - n\varepsilon_0) y.$$

If ε_0 can be negligible for ε_1 and ε_2, this equation is simplified as follows:

$$A = \varepsilon_1 x + \varepsilon_2 y. \tag{15}$$

By combining Eqs. (13), (14) and (15), we have

$$\frac{a}{A_0} = \frac{1}{\varepsilon_2} + \frac{1}{K_1' K_2' \varepsilon_2} \times \frac{1}{b^n} \left(1 + K_1' b - \frac{K_1' ab\varepsilon_1}{A_0}\right). \tag{16}$$

When a is constant, the straight-line relationship will be obtained from Eq. (16) between a/A_0 and $1/b^n$ $(1+K_1'b-K_1' ab\varepsilon_1/A_0)$. Fig. 6 represents the results obtained

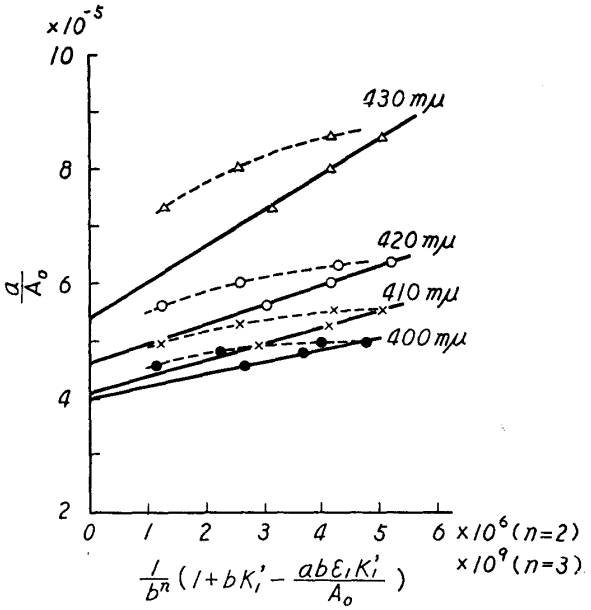

Fig. 6. Relation between a/A_0 and $(1/b^n)(1+bK_1'-ab\varepsilon_1K_1'/A_0)$
at pH 4.17.
Acetone 60%, $NaClO_4$ 0.1 mol/l
U 2.11×10^{-5} mol/l
Flavonol 1.20×10^{-3} mol/l, 1.60×10^{-3} mol/l, 2.40×10^{-3} mol/l

under the condition in which the concentration of uranium was fixed at 2.11×10^{-5} mol/l, the concentration of flavonol was varied as 2.40×10^{-3}, 1.60×10^{-3} and 1.20×10^{-3} mol/l, and pH was fixed at 4.17. In these calculations, K_1' which was corrected for pH was used. From Fig. 6, it is seen that UO_2Fl^+ and UO_2Fl_2 coexist at pH 4.17. From the results, it is clear that the composition of a complex formed at pH 6~7, therefore, is UO_2Fl_2. From Fig. 6, ε_2 at 400 mμ was calculated as 25,100, and K_2' was calculated as $7.6_0\times10^2$ from Eq. (16) and k_2, the formation constant, was calculated as follows:

$$k_2 = \frac{[UO_2Fl_2]}{[UO_2Fl^+][Fl^-]} = \frac{K_2'[H^+]}{K_a} = 9.1_7 \times 10^8.$$

Therefore, the overall formation constant, K, is calculated as follows:

$$K = k_1 k_2 = 2.0_2 \times 10^{19}.$$

3. Complex extracted in TBP-n-hexane

The molecular absorption coefficient of UO_2Fl_2 complex was similar to that of the complex extracted in TBP-n-hexane, but in the absorption curve of UO_2Fl_2, a flat portion was not seen, which was seen in the absorption curve of uranyl-flavonol complex extracted in TBP-n-hexane. Since the coordination number of uranium is known to be eight, it is seen that UO_2Fl_2 can be coordinated with TBP. In order to study the transformation of absorption curves of uranyl-flavonol complex by the addition of TBP, TBP was added to a 60% acetone solution of UO_2Fl_2. As seen from curve 2 in Fig. 7, a flat portion of absorption curve appeared

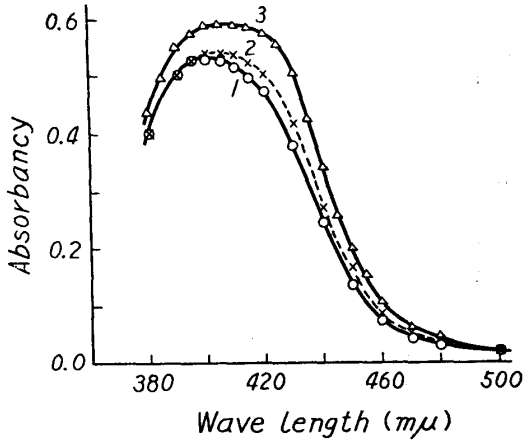

Fig. 7. Absorption curves of uranyl-flavonol chelate.
U 2.11×10^{-5} mol/l
Curve 1. Acetone 60%, $NaClO_4$ 0.1 mol/l without TBP
〃 2. Acetone 60%, $NaClO_4$ 0.1 mol/l, TBP 10%
〃 3. in TBP-n-hexane (1:1) solvent

at 400~410 mμ by the addition of TBP. From the results, it is observed that the uranyl-flavonol complex can be extracted in TBP-n-hexane as $UO_2Fl_2 \cdot n$TBP.

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